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(54) Title: CONSTANT BOILING COMPOSITIONS OF FLUORINATED HYDROCARBONS (57) Abstract Ternary mixtures of pentafluoroethane, difluoromethane and tetrafluoroethane are useful as refrigerants, aerosol propellants, heat transfer media, gaseous dielectrics, fire extinguishing agents, expansion agents for polyolefins and polyurethanes, and as power cycle working fluids.		

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⁺ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

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TITLE
**CONSTANT BOILING COMPOSITIONS OF
FLUORINATED HYDROCARBONS**

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CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of U.S. Application
Serial No. 07/628,000 filed December 17 1990.

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FIELD OF THE INVENTION

This invention relates to constant boiling mixtures for use as refrigerants, aerosol propellants, heat transfer media, gaseous dielectrics, fire extinguishing agents, blowing or expansion agents for polymers such as polyolefins and polyurethanes and as power cycle working fluids. More particularly, it relates to constant boiling mixtures of fluorinated hydrocarbons. Specifically, this invention relates to the use of mixtures of pentafluoroethane (HFC-125), difluoromethane (HFC-32) and tetrafluoroethane (HFC-134 and/or HFC-134a) as replacements for Refrigerant 502 (R-502), a commercial binary azeotrope of chlorodifluoromethane (HCFC-22) and chloropentafluoroethane (CFC-115) and the like that have been used as the refrigerant in numerous commercial applications.

25

BACKGROUND OF THE INVENTION

Recently the long-term environmental effects of chlorofluorocarbons have come under substantial scientific scrutiny. It has been postulated that these chlorine-containing materials decompose in the stratosphere, under the influence of ultraviolet radiation, to release chlorine atoms. Chlorine atoms are theorized to undergo chemical reaction with the ozone layer in the stratosphere. This reaction could deplete or at least reduce the stratospheric ozone layer, thus permitting harmful ultra-violet radiation to penetrate the earth's protective ozone layer. A substantial reduction of the stratospheric ozone layer could have a serious deleterious impact on the quality of life on earth.

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Refrigerant 502, the azeotropic mixture of about 47-50

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5 SUMMARY OF THE INVENTION

 According to the present invention, a ternary fluorocarbon mixture has been discovered that comprises about 5-90 weight percent pentafluoroethane, $\text{CF}_3\text{-CHF}_2$, also known as HFC-125, about 5-90 weight percent difluoromethane, CH_2F_2 , also known as HFC-32, and about 5-90
10 weight percent tetrafluoroethane, $\text{CF}_3\text{-CH}_2\text{F}$ and $\text{CHF}_2\text{-CHF}_2$, also known as HFC-134a and HFC 134, that is suitable for the aforementioned uses, particularly for use in the refrigeration cases found in supermarkets. The substantially constant boiling compositions comprise about 5-59 weight percent HFC-125, 5-59 weight percent HFC-32 and about 5-35 weight
15 percent of at least one of HFC-134 and HFC-134a. The range for HFC-134a is anywhere from about 5-90 weight percent; and, as shown in Table 2, from 15-70 weight percent in mixtures with HFC-125 and HFC-32 were quite satisfactory. As for HFC-134, a range of about 5-45 weight percent, preferably 15-45 weight percent as shown in Table 2, is
20 quite satisfactory.

 The compositions of this invention are particularly useful in refrigeration applications since they maintain their stability and their azeotrope-like properties at temperatures of -30°F to 115°F and pressures of 24 psia to 350 psia as shown in the examples hereinafter. As a matter of
25 information, the compositions of this invention may be used successfully at temperatures as low as -50°F to temperatures as high as 300°F .

 The novel mixture compositions of the instant invention exhibit differences in dew and bubble points. However, these differences can increase the overall energy efficiency of the refrigeration cycle and be
30 beneficial to refrigeration equipment designers.

 There are other ternary and higher blends as shown in Table 2 having desirable characteristics that could be formulated by those skilled in the art from the halocarbons defined and exemplified herein. Another blend that may be formulated for the purposes of this invention is
35 HFC-125/HFC-134a/HFC-134/HFC-32.

 The objective of this description is not to identify every possible blend composition, but to illustrate our discovery of the unexpected properties that the ternary (or higher) blends can take on,

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5 depending on the components and the chosen proportions.

For the purpose of this discussion, "near-azeotropic" is intended to mean essentially azeotropic or essentially constant boiling. In other words, included within the meaning of these terms are variable degrees of near-azeotropic behavior depending on the proportions of the components. As is well recognized in this art, there is a range of compositions which contain the same components as the near-azeotrope and demonstrate equivalent properties at other temperatures and pressures, but will behave essentially as those mentioned.

15 The novel ternary mixtures may be used to produce refrigeration by condensing the mixtures and thereafter evaporating the condensate in the vicinity of a body to be cooled.

The novel mixtures may also be used to produce heat by condensing the refrigerant in the vicinity of the body to be heated and thereafter evaporating the refrigerant.

20 The use of non-azeotropic mixtures that exhibit differences in dew and bubble points can be used with countercurrent heat exchangers to offer potential energy efficiency advantages which pure component and azeotropic and near azeotropic mixtures may not exhibit.

25 The novel mixtures have zero ozone depletion potentials (ODP) compared with Refrigerant 502. The ODP are provided in Table 1 for comparison.

30 The novel mixtures have little effect on the global warming potential. The global warming potentials (GWP) of the mixtures/components are listed in Table 1 and R-502 is provided for comparison.

TABLE 1

<u>Refrigerant</u>	<u>Chemical Formula</u>	<u>ODP</u>	<u>GWP</u>
R-502	$\text{CHClF}_2/\text{CClF}_2\text{CF}_3$.25	5.1
35 HFC-125	CHF_2CF_3	.0	.65
HFC-134a	$\text{CF}_3\text{CH}_2\text{F}$.0	.29
HFC-134	CHF_2CHF_2	.0	.15
HFC-32	CH_2F_2	.0	.15

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Also, the mixtures can be formulated such that the initial composition or the composition during leakage remains nonflammable. By "nonflammable" is meant a gas mixture in air which will not burn when subjected to a spark igniter according to Flammability Test Method ASTM-E681-85.

10

It should be understood that one or more of the compounds shown in Table 2 can be substituted or combined with the substantially constant boiling ternary mixtures of this invention to provide additional substantially constant boiling mixtures for similar uses while adding advantageous properties unique to the added component(s).

15

TABLE 2

	<u>Nomenclature</u>	<u>Chemical Formula</u>
	HFC-22	CHClF_2
20	HFC-143a	CH_3CF_3
	HFC-161	CH_2FCH_3
	FC-218	$\text{CF}_3\text{CF}_2\text{CF}_3$
	Propane	$\text{CH}_3\text{CH}_2\text{CH}_3$
	HFC-23	CHF_3
25	HFC-227ea	$\text{CF}_3\text{CHF}_2\text{CF}_3$

The invention will be more clearly understood by referring to the examples which follow.

30

EXAMPLES 1-12

Evaluation of the refrigeration properties of the novel ternary mixtures of the invention versus Refrigerant 502 are shown in Table 3. The data were generated on a one-ton basis, i.e., based on the removal of heat from a space at the rate of 12,000 BTU/hr.

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TABLE 3

Comparison of Refrigeration Performance

10	<u>Conditions</u>							Net Refrig. Effect	<u>Ex</u>
	<u>Evaporator</u>			<u>Condenser</u>					
	<u>Temp</u>			<u>Temp.</u>					
	<u>In</u>	<u>Out</u>	<u>Pres.</u>	<u>In</u>	<u>Out</u>	<u>Pres.</u>			
	<u>(°F)</u>	<u>(°F)</u>	<u>(psia)</u>	<u>(°F)</u>	<u>(°F)</u>	<u>(psia)</u>			
<u>Refrigerants</u>	<u>(°F)</u>	<u>(°F)</u>	<u>(psia)</u>	<u>(°F)</u>	<u>(°F)</u>	<u>(psia)</u>	<u>C.O.P.</u>	<u>(BTU/lb)</u>	
R-502	-30	-30	24.0	115	115	281.9	1.89	46.7	Control

Mixtures

15 125/134a/32

(wt.%)

	45/45/10	-34	-25	18.5	119	112	264.3	1.93	68.5	1
	75/15/10	-32	-28	24.5	117	113	318.3	1.80	50.0	2
	18/57/25	-36	-25	18.6	120	111	270.1	1.97	73.2	3
20	25/25/50	-34	-27	26.6	117	112	350.3	1.86	81.7	4
	50/30/10	-34	-26	21.1	118	112	286.9	1.87	74.2	5
	10/70/20	-36	-25	16.9	120	111	244.5	2.01	73.1	6

Mixtures

25 125/134/32

(wt.%)

	45/45/10	-38	-23	16.5	121	109	250.1	1.95	61.7	7
	75/15/10	-33	-27	24.0	117	113	315.7	1.80	50.8	8
	18/57/25	-39	-21	16.0	123	108	246.7	2.01	77.9	9
30	25/25/50	-36	-25	24.5	119	111	337.9	1.87	84.2	10
	50/30/10	-36	-25	19.7	119	111	281.7	1.87	56.1	11
	10/70/20	-39	-21	13.6	123	108	216.8	2.07	78.8	12

35 "Coefficient of Performance" (COP) is the ratio of net refrigeration effect to the compressor work. It is a measure of refrigerant energy efficiency.

"Net Refrigeration Effect" is the change in enthalpy of the refrigerant in the evaporator, i.e., the heat removed by the refrigerant in

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5 the evaporator.

For a refrigeration cycle typified by the above conditions, the COP of the mixtures are either significantly higher or essentially the same as R-502. These mixtures exhibit temperature glides (difference in inlet and exit temperature) through the condenser and evaporator. These glides in temperature vary from 3 to 18°F, depending on the composition of the mixture. In the case of an azeotrope the temperature glide is 0, in the case of a near-azeotropic mixture a temperature glide may be as much as 10°F. However, these temperature glides should not pose any significant problems to equipment manufacturers. In fact, higher temperature glides may be useful to aid designers increase the energy efficiency of their machines. Also, the mixtures have much more capacity than R-502, due to their higher vapor pressures.

Additives such as lubricants, corrosion inhibitors, stabilizers, dyes and other appropriate materials may be added to the novel compositions of the invention for a variety of purposes provided they do not have an adverse influence on the composition for their intended applications.

In addition to refrigeration applications, the novel constant boiling compositions of the invention are also useful as: aerosol propellants, heat transfer media, gaseous dielectrics, fire extinguishing agents, expansion agents for polymers such as polyolefins and polyurethanes, and power cycle working fluids.

EXAMPLE 13

30 A phase study was made on pentafluoroethane, tetrafluoroethane and difluoromethane to verify the fractionation and change in vapor pressure during a phase change from liquid to vapor.

Blends were prepared in 75 cc stainless steel cylinders consisting of pentafluoroethane, 1,1,1,2-tetrafluoroethane, and difluoromethane. The cylinders were agitated with a magnetic stirrer and submerged in a constant temperature bath at 23.8°C. The vapor pressure was constantly measured using a pressure transducer and the vapor composition was sampled at various times during the experiment and

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5 analyzed using a standard gas chromatography method. Initial and final liquid concentrations were also analyzed by gas chromatography. Initial liquid (IQ), final liquid (FQ), vapor composition and vapor pressure data recorded in Tables 4, 5 and 6.

10

TABLE 4

	<u>Sample</u>	<u>Percent Loss</u>	<u>Composition (wt.%)</u>			<u>Vapor Pressure</u>	
			<u>HFC-125</u>	<u>HFC-134a</u>	<u>HFC-32</u>	<u>(psia)</u>	<u>(% Change)</u>
	IQ	0	48.8	17.3	33.9	207.2	0
15	1	6.3	51.0	4.3	44.6	206.0	0.6
	2	12.5	51.8	7.1	41.1	204.8	1.2
	3	18.8	50.9	8.6	40.5	203.6	1.7
	4	25.0	50.9	9.5	39.7	202.2	2.4
	5	31.3	50.6	10.7	38.7	200.5	3.2
20	6	37.5	50.6	11.2	38.1	198.5	4.2
	7	43.8	50.6	12.0	37.5	196.5	5.2
	8	50.4	50.6	12.2	37.2	193.7	6.5
	FQ	50.4	49.4	22.0	28.6	193.7	6.5

25

TABLE 5

	<u>Sample</u>	<u>Percent Loss</u>	<u>Composition (wt.%)</u>			<u>Vapor Pressure</u>	
			<u>HFC-125</u>	<u>HFC-134a</u>	<u>HFC-32</u>	<u>(psia)</u>	<u>(% Change)</u>
	IQ	0	33.9	38.2	27.9	188.4	0
30	1	8.3	41.2	18.8	39.5	184.1	2.3
	2	16.7	40.9	21.9	37.3	180.8	4.0
	3	25.0	40.2	24.0	35.7	178.3	5.4
	4	33.0	38.9	25.3	35.0	174.0	7.6
	5	41.8	37.4	30.3	32.3	171.2	9.1
35	6	51.0	37.3	32.5	30.2	168.7	10.4
	FQ	51.0	30.2	47.0	22.7	168.7	10.4

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TABLE 6

	Sample	Percent Loss	Composition (wt.%)			Vapor Pressure	
			HFC-125	HFC-134a	HFC-32	(psia)	(% Change)
	IQ	0	18.7	56.4	24.8	173.2	0
10	1	1.7	26.5	36.9	36.6	172.1	0.4
	2	6.2	25.5	37.5	37.0	169.7	1.4
	3	10.6	25.3	38.5	36.2	164.5	2.4
	4	15.1	24.8	40.2	35.5	162.5	3.5
	5	19.6	24.2	41.6	34.3	160.1	4.5
15	6	24.4	24.4	40.9	34.6	158.4	5.7
	7	28.9	23.8	42.8	31.3	155.6	7.1
	8	33.3	22.8	45.9	31.3	154.0	8.4
	9	37.8	23.1	45.7	31.2	151.3	9.8
	10	42.2	23.4	46.3	31.6	149.0	11.2
20	11	46.7	20.8	49.7	29.5	146.3	12.8
	12	48.9	21.1	51.8	27.1	144.1	13.8
	13	54.4	21.4	51.3	27.3	140.2	15.8
	FQ	54.4	12.7	73.1	14.2	140.2	15.8

25 These data (Tables 4-6) demonstrate that with more than
 50% of the original charge depleted, the vapor pressure has changed less
 than 16% in all cases. The degree of fractionation depends on the tetra-
 fluoroethane concentration and can be adjusted to give small changes in
 vapor pressure. Mixtures containing 35 wt.% of 1,1,1,2-tetrafluoroethane
 30 (HFC-134a) or less are considered substantially constant boiling since the
 vapor pressure will change less than 10% at 50% leakage. Mixtures
 containing greater than 35 wt.% of 1,1,1,2-tetrafluoroethane are considered
 non-azeotropic as the vapor pressure has changed more than 10% at 50%
 leakage. These mixtures could still be quite useful in many applications,
 35 especially those that require very small sizes. At small charge sizes,
 recharging the mixture due to vapor leakage to return to the desired
 composition does not pose any significant problem. Substituting 1,1,2,2-
 tetrafluoroethane (HFC-134) for HFC-134a would be expected to give

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5 similar results at lower HFC-134 concentrations.

These data also demonstrate that, even though the mixtures fractionate and the vapor pressure decreases, the difluoromethane concentration in both the liquid and vapor phases during leakage also decreases. Therefore, the blend will not become flammable if the initial
10 concentration is nonflammable. Similar behavior is predicted for the mixture containing HFC-134 instead of HFC-134a.

EXAMPLE 14

The ozone depletion potential is based on the ratio of
15 calculated ozone depletion in the stratosphere resulting from the emission of a compound compared to the ozone depletion potential resulting from the same ratio of emission of CFC-11 which is set at 1.0. A method of calculating ozone depletion potential is described in "The Relative Efficiency of a Number of Halocarbons for Destroying Stratospheric
20 Ozone", by D. J. Wuebbles, Lawrence Livermore Laboratory Report UCID-18924, January, 1981, and "Chlorocarbon Emission Scenarios: Potential Impact on Stratospheric Ozone", by D. J. Wuebbles, Journal Geophysics Research, 88,1433-1443, 1983.

HFC-125 ($\text{CF}_3\text{CF}_2\text{H}$), HFC-134a (CF_3CFH_2) or HFC-134
25 ($\text{CF}_2\text{HCF}_2\text{H}$), and HFC-32 (CF_2H_2) contain no chlorine atoms; therefore, they have no ozone depletion potential (0 ODP).

The global warming potentials (GWP) of the fluorocarbons were determined using the method described in the "Scientific Assessment of Stratospheric Ozone: 1989", sponsored by the U.N. Environment
30 Programme. The GWP is a phenomenon that occurs in the stratosphere. It is calculated using a model that incorporates parameters based on the agent's atmospheric lifetime and its infra-red cross-section or its infra-red absorption strength per mole as measured with an infra-red spectrophotometer.

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CLAIMS:

1. A ternary fluorocarbon mixture comprising about 5-90
weight percent pentafluoroethane, about 5-90 weight percent difluoro-
methane and 5-90 weight percent of at least one tetrafluoroethane.

2. A ternary fluorocarbon mixture as in Claim 1 which
contains 1,2,2,2-tetrafluoroethane and 1,1,2,2-tetrafluoroethane.

3. A mixture as in Claim 1 comprising about 5-59 weight
percent pentafluoroethane, about 5-59 weight percent difluoromethane and
about 36-65 weight percent of at least one tetrafluoroethane.

4. A substantially constant boiling mixture as in Claim 1
comprising about 5-59 weight percent pentafluoroethane, about 5-59 weight
percent difluoromethane and about 5-35 weight percent of at least one
tetrafluoroethane.

5. A process for producing refrigeration comprising the steps
of condensing the mixture of Claim 1 and, thereafter, evaporating said
mixture in the vicinity of a body to be cooled.

6. A process for producing heat comprising the steps of
condensing the mixture of Claim 1 in the vicinity of a body to be heated
and, thereafter, evaporating said mixture.

7. A process for heating or cooling comprising the step of
using the mixture of Claim 1 as a heat transfer media.

8. A process for atomizing a fluid comprising the step of
using the mixture of Claim 1 as an aerosol propellant.

9. A process for electrically insulating comprising a step of

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5 using the mixture of Claim 1 as a gaseous dielectric.

10. A process for suppressing a fire comprising a step of using the mixture of Claim 1 as a fire extinguishing agent.

10 11. A process for producing a foamed polymer comprising a step of using the mixture of Claim 1 as a foam expansion agent.

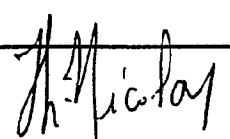
12. A process for delivering power comprising a step of using the mixture of Claim 1 as a power cycle working fluid.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/09150

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C09K5/04; C09K3/30		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C09K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
P,X	US,A,4 978 467 (SHANKLAND) 18 December 1990 see abstract; claims 1,2,5,8; examples 2,4 ---	1-7,12
X	EP,A,0 400 894 (DU PONT DE NEMOURS) 5 December 1990 see page 3, line 51 - page 4, line 5; claims 1-4 see abstract ---	1-7,12
P,X	EP,A,0 430 169 (MATSUSHITA) 5 June 1991 see claims 1-3; figures 7,8; tables 7,8 ---	1-7,12
P,X	WO,A,9 109 090 (DU PONT DE NEMOURS) 27 June 1991 see page 8, line 10 - page 9, line 9; claims 1,2 ---	1-7,12
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
01 APRIL 1992	10. 04. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	NICOLAS H. J. F. 	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9109150
SA 54939**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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